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Research Article

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# The Removal of Iron from Landfill Leachateby Rice Husk Packed Bed Column

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**ABSTRACT**

Rice husk and its modified forms have been proven effective in reducing pollutants from water and wastewater, including metals and non metals. But, to date, only few studies have focused on landfill leachate. Landfill leachates may contain large amounts of organic matter where humic-type constituents consist an important group, as well as ammonia-nitrogen, heavy metals, chlorinated organic and inorganic salts. Iron were found in significant quantities metal at the landfill site. This study purposes to investigate the ability of rice husk to reduce Iron (Fe) from landfill leachate. Landfill leachate was pumped and filled by gravity into the rice husk packed bed column. The effect of influent flow rate to adsorption capacity was studied by varying flow rate of 5 mL/min and 10 mL/min. The effluent-influent concentration ratio $C_e/C_0$ (%) as a function of throughput volume (L) was used to represent the breakthrough curve in column systems. Result shows that the flow rate of 5 mL/min was favorable to achieve higher removal rates with the percentage of iron was 64%.At breakthrough time, the iron effluent concentration reached on 0.571 and 1.903 mg/L for flow rate of 5 mL/min and 10 mL/min respectively.

**Keywords :** Rice husk, Packed bed column, Iron, Landfill leachate

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## INTRODUCTION

Landfill often cause problems due to lack of management. Landfill leachate for instance, a liquid which is formed by leaching process of disposal waste then percolating or infiltrating into groundwater then to surface water, can contaminate groundwater, soil and surface water. It contains complex contaminants including organic matter (both biodegradable and non-biodegradable carbon), ammonia-nitrogen, heavy metals, chlorine organic and inorganic salts. Iron generated by domestical and industrial waste is common heavy metal found in landfill leachate.

Thus, it is a challenge to find appropriate treatment to reduce contaminat on landfill leachate. Due to its compelexicity contaminants, combined treatment of physical, chemical, and biological have been usually used to improve the treatment efficiency of landfill leachate[8,17]. Physico-chemical treatment has been found to be suitable not only for the removal of heavy metals from landfill leachate, but also for refining of biologically treated leachate [9]. Adsorption is a common method used in physical-chemical treatment. This method has been studied on batch scale experiment and column experiment [1-2, 4-6, 9-15,17-24].

Some findings on leachate treatment using rice husk as adsorbent has been reported. It was reported that column filled with rice husk can eliminate heavy metals. Furthermore, the behaviour of column in these studies noted that adsorption capacities occurs significantly [15,20,22]. Similar reports related to use of rice husk as adsorbent also stated that rice husk was considerably used in adsorption process [1-4, 6,7, 11-14, 16-20, 23, 24]. Besides, its local availability, rice husk also has high mechanical strength, granular structure, chemical stability, water insolubility, and low production cost [11].

This research was purposed to investigate the behaviour of packed bed column filled with rice husk, which was designated as rice husk packed bed column to reduce iron in landfill leachate. Further, the effects of varying flow rate as determinant factors influencing the adsorption process were also studied.

## EXPERIMENTAL SECTION

### 2.1. Preparation of Rice Husk

Raw rice husk was collected from local rice mill in Kuala Selangor, Malaysia. It was firstly washed several times with tap water continued with distilled water to remove dirt particles and impurities. Then to remove moisture and impurities, it was dried at 100$^o$C for 4 hours until the weight of rice husk become constant. Finally, it was ground withgrinder machine (National MK 110 food processor) and sieved to homogenous particle size less than 600 µm. Thereafter, the sieved rice husk was preserved in air tight container at room temperature to be used.

### 2.2. Landfill LeachateSample

Leachategenerated at Landfill of Core Competition Company, "Sungai Kembong", Semenyih, Kuala Selangor was used as leachate sample source. Sample was taken randomly by grab method for several times. The characteristic of collected leachate was analyzed immediately and preserved in refrigerator at 2$^o$C temperature. Concentration of iron was one of the highest concentration of heavy metals contained in collected leachate, as shown clearly in Table 1.

The value of pH was measured by Hanna pH meter while the temperature was checked by thermometer. COD was analyzed using closed reflux method and then measured by spectrophotometer. Fe was analyzed by by inductively couple plasma atomic electronic spectrophotometer (ICP-OES) (Perkin Elmer, Model: Optima 3000). But before Fe analyzing, sample of leachate was homogenized by shaking on plate stirred then filtered using Laboratory Scheleicher&Schuell model filter paper from Germany with 0.45 µm pore size and 47 mm diameter.

**Table 1: Composition of Landfill Leachate Sample**

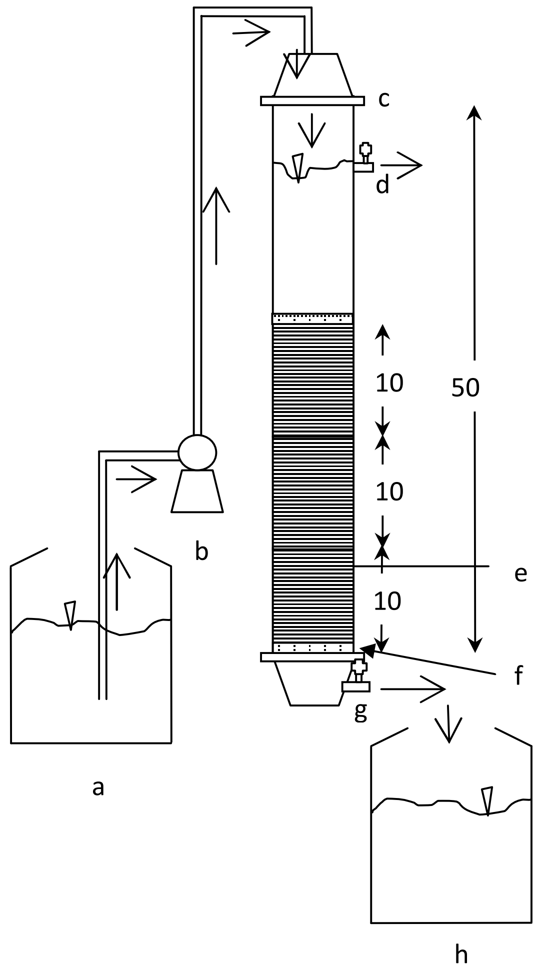
| Parameter | Unit | Value | Average |
|---|---|---|---|
| pH | | 7.15 - 7.98 | 7.74 |
| COD | mg/L | 9000 - 15600 | 11300 |
| Temperature | $^o$C | 27 – 28 | 27.6 |
| Al | mg/L | 0.13 - 2.724 | 1.264 |
| Cd | mg/L | 0.228 - 105.73 | 29.4 |
| Cr | mg/L | 0.02 - 0.0675 | 0.017 |
| Cu | mg/L | 0.0237 - 0.168 | 0.061 |
| Fe | mg/L | 0.1925 - 14.428 | 5.622 |
| Mn | mg/L | 0.065 - 0.758 | 0.450 |
| Ni | mg/L | 0 - 0.586 | 0.121 |
| Pb | mg/L | 0 - 0.399 | 0.067 |
| Zn | mg/L | 0.0725 - 5.927 | 1.463 |

### 2.3. Characterization of Rice Husk

Mineral composition and morphological features of rice husk were identified by XRD, a Siemens D-5000 system with Cu Kα radiation over 2θ from 5$^o$ to 80$^o$ at a rate of 0.05$^o$/second with range of wavelength 1.5406 Å and a step time of 2 seconds. Morphological characteristics of rice husk were examined by SEM (A Philip XL30 scanning electron microscope in secondary electron mode, equipped with energy dispersive X-ray, JEOL6335F-SEM, Japan). The presence of functional groups in rice husk was identified by (Thermo nicolet, Model Magna 760). It was conducted at room temperature, using Pellet (pressed-disk) technique and chosen spectral range of 4000 to 400 cm$^{-1}$. BET surface area, average pore diameter and total pore volume of the supports as well as the catalysts were determined by nitrogen adsorption–desorption isotherm at 77.35K using the BET method in a MicromeriticsAccusorb 2000 apparatus. Before measurement, each sample was degassed at 473K for 4 h.

### 2.4. Preparation of Column

Column used in research (Figure 1) was made of a vertical cylindrical Perspex column with a depth of 50 cm and diameter of 5 cm. The bottom of cone-shaped column has a height of 5 cm and a divergence angle of 15$^o$. The column was filled with rice husk to the certain high. The height of filled rice husk determined the dosage of rice husk.




Legend

a. Influent wastewater tank
b. Influent feed pump
c. Perforated plate
d. Overflow valve
e. Adsorbent
f. Perforated polymer
g. Effluent wastewater valve
h. Effluent wastewater tank

**Figure 1. Experimental setup for column studies**

The rice husk was packed and supported by two perforated polymer. The column also supported with two perforated plastic plates. One was put on the top of column to distribute landfill leachate onto the surface of adsorbent and to keep flow rate constant. The other one was put on the bottom of column to prevent the adsorbent from leaching and clogging into the drainage area. Leachate influent was introduced to column by BT300-2J peristaltic pumps (Baoding Longer Precision Pump CO., Ltd). The column was also equipped with 1 overflow valve to avoid the over limit of sample in case the clogging and saturation occurs in reactor and 1 outlet valve to collect sample. The column was designated as rice husk packed bed column.

### 2.5. Behaviour of Rice Husk Packed BedColumn

Leachate was feed into column by pumping. It was then flowing down through column by gravity force. The adsorption process occurs in rice husk bed which installed in column. Experiments were done at room temperature (range of $25^oC$ – $27^oC$). The effluent samples were collected in regular time for every one hour and stored in dark cool refrigerator for analysis. The effect of leachate flow rate to adsorption capacity was studied by 5 mL/min and 10 mL/min.The sample was collected every one hour and more frequent than in the following days to evaluate changes of iron concentration trend

Adsorption capacity of column was observed by breakthrough curve illustration. It was calculated from of differences value between the influent and effluent concentration in column. The volumetric throughput to reach breakthrough and shape of the breakthrough curve are also used to determine the operation and the dynamic response of an adsorption column. It is normalized as the ratio of effluent metal concentration to inlet metal concentration ($C_e/C_o$) and computed as a function of time or volume of effluent for a given bed depth. Effluent volume ($V_e$) can be calculated from Eq. (1):effluent-influent concentration ratio $C_e/C_0$ (%) as a function of throughput volume (L).

$$V_e = Qt_{tot} \quad \text{Eq. (1)}$$

Here $t_{tot}$is the total flow time (min) and Q is the volumetric flow rate (mL/min). The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration (Cad; mg/L) versus *t* (min) plot can be used to find the total adsorbed metal quantity (maximum column capacity). Total adsorbed metal quantity ($q_{tot}$; mg) in the column for a given feed concentration and flow rate (*Q*) is calculated from Eq. (2):

$$q_{tot} = \frac{QA}{1000} = \frac{Q}{1000}\int_{to}^{te} C_{ad}\,dt \quad \text{Eq. (2)}$$

Total amount of leach q. (3):

$$M_{tot} = \frac{C_o Q t_{tot}}{1000} \quad \text{Eq. (3)}$$

Total removal is calculated from Eq. (

$$TotalRemoval(\%) = \frac{q_{tot}}{M_{tot}} * 100 \quad \text{Eq. (4)}$$

Equilibrium metal uptake ($q_{eq}$) in the column (or maximum capacity of the column) is defined by Eq. (5) as the total amount of metal adsorbed ($q_{tot}$) per gram of adsorbent (m) at the end of total flow time:

$$q_{eq} = \frac{q_{tot}}{m} \quad \text{Eq. (5)}$$

## RESULTS AND DISCUSSION

### 3.1.Characterization of Rice Husk

Table 2 shows physical characteristics of rice husk. The value of pH was 6.670 and bulk density was 0.477 kg/m$^3$). The value of surface area, micropore area and total volume pore of rice husk were high enough to provide space for storing more adsorbate molecules. In other words, the adsorption process of landfill leachate was kept running well [6].

**Table 2: Physical characteristics of rice husk**

| Parameter | Unit | Rice husk |
|---|---|---|
| Bulk density | kg/m$^3$ | 0.447 |
| Particle size | µm | ≤ 600 |
| moisture content | % | 8.955 |
| BET surface area | m$^2$/g | 4.093 |
| Langmuir surface area | m$^2$/g | 139 |
| Micropore area | m$^2$/g | 2.175 |
| Average pore diameter | µm | 71.8 |
| Total pore volume | cm$^3$/g | 0.007 |
| Micropore volume | cm$^3$/g | 0.001 |
| Average pH | - | 6.67 |

TheXRDplots of raw rice husk are shown in Figure 2. The XRD analysisnoted that rice husk has two broad peaks. The peaks from 15 to 35-2θdiffraction angles indicates the existence of amorphous silica.

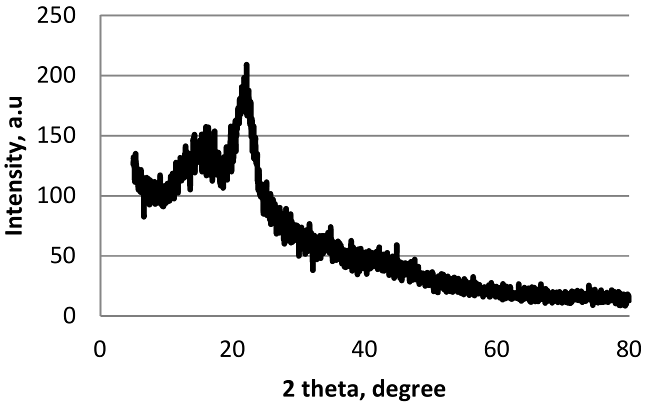



**Figure 2. XRD – analysis for rice husk**

This result confirms the previous report [10]. Silica existing in rice husk have significant function to keep adsorption process run well as reported by [12] and [14].

Morphology of the rice husk was verified with SEM in certain magnificent as shown in Figure 3. The figure 3, before (a) and after (b) adsorption process shows quite different. The figure 3 (a) configures aligned bumps composed mainly of silica onto the cellulose. Meanwhile, the surface of rice husk adsorbent after adsorption process (figure 3.(b)) was fulfilled with the uptake iron reflected with the particle agglomeration onto adsorbent surface.

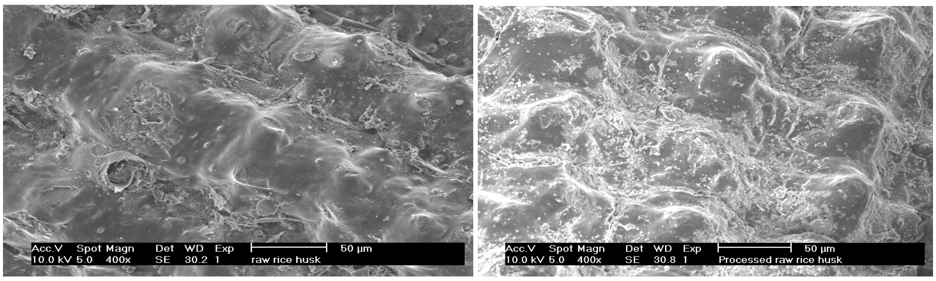


**Figure 3.SEM analysis of adsorbent (a) before and (b) after adsorption process.**

According to the results of FTIR, curve of rice husk (Figure 4)emphasizes the results obtained in XRD and SEM. The peaks observed detects the presence of Si–O, Si–H, Si–C, –CH and –OH bond groups on the rice husk surface. The peak was observedat about 651 – 740 $cm^{-1}$ could be assigned to the phenyl groups C-H. The peak around 1630 $cm^{-1}$ corresponds to C=O stretch. The alkene was observed at the peaks of 1920 and 2030 $cm^{-1}$. Other broad peaks between 3020 and 3290 $cm^{-1}$ in rice husk were also observed that were attributed to – OH bond. The bonds of Si–O, Si–H, Si–C, –CH and –OH are attributed to adsorption process [11].

### 3.3 Packed Bed Column Study

The raw landfill leachate was composed of iron concentrations of 4.584 and 14.427 mg/L. Iron adsorption capacity and its removal was shown in Table 4 which was was determined based on iron concentrations entering the column. Removal of iron reached on 63.805% at flow rate of 5 mL/min, higher than percentage of removal obtained at flow rate of 10 mL/min (44.254%). It notes that lower flow rate is better in adsorption process.

The breakthrough curve of iron adsorption illustrated in Figure 5 for both of flow rates also emphasizes the previous statement. The results also indicate that higher flow rate accelerates bed exhaustion. The column with flow rate of 10 mL/min, for iron and cadmium was exhausted or saturated (Ce/Co > 95 %) after 46.2 L throughput volume, earlier than flow rate of 5 mL/min. It was discovered that columns clogging occurred at flow rate of 10 mL/min after 58.8 L throughput volume or after three days of column operation. For 5 mL/min flow rate, the clogging did not occur even after six days of column operation. Li [5] also reported that the clogging in his column operation reaching after 7 days operation with low flow rate. The existence of biofilm which illustrate biological activity arround adsorbent surface in column assumed did not impact on adsorption capacity.

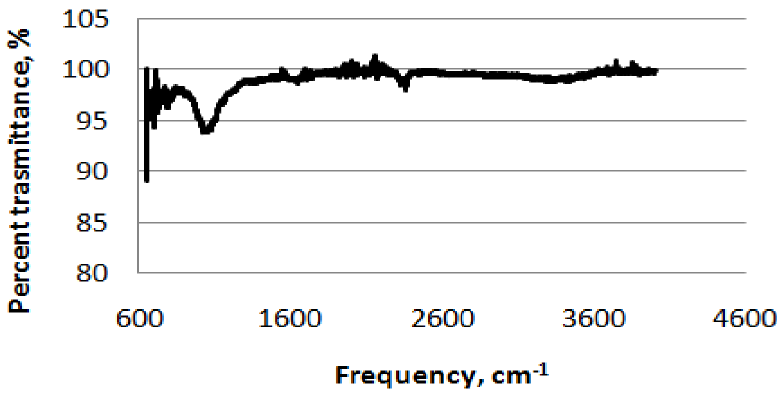



**Figure 4. FTIR analysis for virgin rice husk**

**Table 4: The total adsorbed quantity ($q_{tot}$), equilibrium uptake ($q_{eq}$), total amount of metal ion through column ($M_{tot}$) and total removal percentage for iron adsorption from landfill leachate at RRH packed bed column**

| Q (mL/min) | $t_{tot}$ (min) | Co (mg/L) | Sum of integration | $q_{total}$ (mg) | $q_{eq}$ (mg/g) | $m_{tot}$ (mg) | Removal (%) |
|---|---|---|---|---|---|---|---|
| 5 | 9600 | 4.584 | 6125.248 | 140.391 | 0.624 | 220.032 | 63.805 |
| 10 | 5880 | 14.427 | 2602.127 | 375.400 | 1.668 | 848.288 | 44.254 |

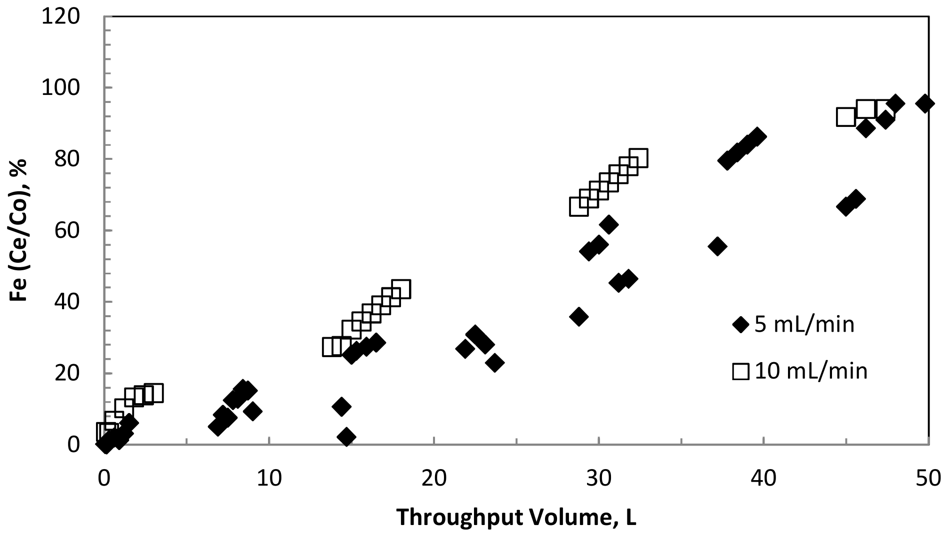



**Fig.5.The experimental breakthrough curves for adsorption of cadmium from landfill leachate onto rice husk packed bed column at as a function of throughput volume in different flow rate.**

According to Table 5, at breakthrough time, the effluent of iron was reached at 0.571 and 1.903 mg/L for flow rate of 5 mL/min and 10 mL/min respectively. Obviously, table 5 shows only in flow rate of 5 mL/min, the effluent of iron can be reduced lower than standardized acceptable concentration of the Malaysian Environmental Quality Act 1974 (EQA 1974) for discharge landfill leachate. While, at saturated condition time, the effluent of iron for both of flow rates closed to the influent of iron.

**Table 5: The comparison of influent, effluent and threshold limit value of EQA**

| | Flow rate 5 mL/min | Flow rate 10 mL/min |
|---|---|---|
| Influent(mg/L) | 4.584 | 14.427 |
| Effluent at breakthrough time (mg/L) | 0.571 | 1.903 |
| Effluent at saturated time (mg/L) | 4.38 | 14.215 |
| Environmental quality act 1974 (mg/L) | 5 | 5 |

The breakthrough condition indicates that the rice husk adsorbent could be regenerated to prevent the saturated condition which led to the increasing of final effluent concentration [8]. It noted with the increasing of Ce/Co ratio (>95%).

## CONCLUSION

Based on the results of experiments can be concluded as follows:

1. The rice husk packed bed column is favourable to reduce iron concentration from landfill leachate.
2. Flow rate has significat effects on iron adsorption removal. The highest percentage removal achieved at flow rate 5 mL/min was 63.805%.
3. Flow rate of 5 mL/min has longer life span. The saturated of column occurred faster in flow rate 10 mL/min, even in this flow rate the clogging fallen after 58.8 L throughput volume. However, at flow rate 5 mL/min, the clogging of column in was still not detected even after 6 days operation.
4. Compared to the Malaysian Environmental Quality Act (1974), only at flow rate of 5 mL/min, iron concentration at breakthrought time was lower than that of threshold limit value of iron concentration standardized by EQA 1974.

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## REFERENCES

[1] AAM Daifullah; NS Awwad; SA El-Reefy, *Chemical Engineering and Processing*,**2004**,43: 193-201.
[2] AH Mahvi; N Alavi; A Maleki, *Pak. J. Bio. Sci*., **2005**, 8(5): 721–725.
[3] AH Robinson,Landfill leachate treatment: An article based on a paper with the same title, which was presented at the 5th international Conference on Membrane Bioreactors (MBR5); 9 pp, **2004**
[4] AK Bhattacharya; TK Naiya; S N Mandal; SK Das, *Chem. Eng. J.* , **2008**, 137: 529–541.
[5] C Li, Aqueous solutions and synthetic landfill Leachate using low-cost natural adsorbents. Thesis of Master of Science (Engineering). Canada: Queen's University Kingston, **2008**
[6] CR Teixeira Tarlye; MA Zezzi Arruda, *Chemosphere*, **2004**, 54: 987 - 995.
[7] D Duong, *Adsorption analysis: equilibria and kinetics*. London: Imperial College Press, **1998**
[8] D Zhou; L Zhang; J Zhou; S Guo, *Journal of Applied Polymer Science*, **2004**, 94: 684 - 691.
[9] E Tinamaz; A Ongen, **2006**, Risks posed by unsanitary landfill leachate to groundwater quality. In: Tellam, J.H. et al. (Eds.), *Nato Science Series Vol. 74: Urban Groundwater Management and Sustainability*. Netherland: Springer Publisher (pp. 259–268).
[10] F Kargı; MY Pamukoglu, *Bioresource Technology*, **2004**, 94: 285-291.
[11] G Sreejalekshmi; KA Krishnan; TS Anirudhan, *J. Haz. Mat.*,**2009**, 161: 1506–1513.
[12] J Qi; Z Li; Y Guo; H Xu, *Mat. Che. Phys. J*., **2004**, 87: 96–101.
[13] JN Sahu; S Agarwal; BC Meikap; MN Biswas, *Haz. Waste Mat*., **2009**, 161: 317 – 324.
[14] M Akhtar et al., *J. Haz. Mat*.,**2006**,B128, 44–52.
[15] M Kasman; S Ibrahim; Salmariza. *Jurnal Litbang Industri*, **2014**, 4 (1): 9 – 17.
[16] Ministry of Natural Resources and Environment, *Akta Kualiti Alam Sekitar* (*Environmental Quality Act*). Kualu Lumpur, Malaysia, **1974**
[17] MMD Zulkali; AL Ahmad; NH Norulakmal, *Bioresource Technology*, **2006**, 97: 21-25.
[18] N R Bishnoi, M Bajaj; N Sharma; S Gupta, *Bioresource Technology*, **2004**, 91(3): 305-307.
[19] Q Feng; Q Lin; F Gong; S Shuici; M Shoya, *Journal of Colloid and Interface Science*, 2004, 278: 1-8.
[20] S Mohan; G Sreelakshmi, *J. Haz. Waste Mat.*, **2008**, 153: 75–82.
[21] SH Lin; CC Chang, *J. Water Res*., **2000**, 34: 4243–4249.
[22] U Kumar; M Bandyopadhyay, *J. Haz. Waste Mat*., **2006**, B129: 253 – 259.

[23] V Ponnusami; V Krithika; R Madhuram; SN Srivastava, *Journal Hazardous Materials*,**2007**,142: 397–403.
[24] VC Srivastava; ID Mall; IM Mishra, *Chemical Engineering Journal*, **2008**,140: 136-144.